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TEKTITE COMPOSITIONAL TRENDS AND EXPERIMENTAL VAPOR FRACTIONATION OF SILICATES

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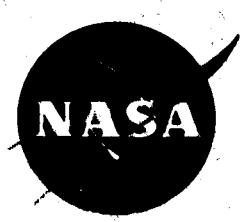

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TEKTITE COMPOSITIONAL TRENDS AND EXPERIMENTAL VAPOR FRACTIONATION OF SILICATES

by

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ABSTRACT

Recent observations indicate that Muong Nong type tektites, which are highly structured, contain coesite and have a high silica content, may be primary tektite material. High-temperature experiments at atmospheric pressure show that, starting with material of this composition, vapor fractionation results in a residuum which follows the compositional trends of tektites in general. There is a significant difference between the tektite trends and those produced in experiments under reducing conditions.

INTRODUCTION

Recently, several authors have discussed the importance of high temperature selective volatilization in the formation of tektites. This process has certainly been involved in the formation of these glassy objects. The frothing of lechatelierite, which is viscous even at high temperatures, and the dissociation of zircon to baddeleyite (Clarke and Wosinski, 1967) are indications that tektites were formed at temperatures much higher than those attained in ordinary terrestrial processes. In addition, the proposed mechanisms of origin involve extremely high temperatures. Temperatures at which extreme volatilization can take place can be achieved either in the case of a meteorite impact or during entry of a large parent body into the earth's atmosphere.

In the past, investigations on the role of this process in the formation of tektites have involved both high temperature experiments and the compositional analysis of tektites. A summary of this work has been presented by Philpotts and Pinson (1966) and an enlarged discussion of the problem was presented by Schnetzler and Pinson (1963). Cohen (1960) proposed volatilization to explain the differential loss of germanium from australite flanges. Philpotts and Pinson (1966) used the variable Rb/Sr ratio in moldavites as an indicator of fractionation and were able to explain many of the compositional variations on the basis of vapor fractionation. They concluded that it is difficult for any other process to explain the observed compositional relationships.

The results of experimental studies have been published by Lovering (1960), Friedman et al. (1960) and Walter and Carron (1964). In these cases, however, the degree of fractionation was insufficient to permit definitive statements on the fractionation trends. Lovering's experiments, carried out in a solar furnace, were limited to a maximum temperature of about 2000°C. He used

granite as a starting material. The results of the chemical analyses showed that SiO_2 dropped from 75.96% in the starting material to 75.48%, but such a small loss may not have been significant.

Friedman et al. (1960) used several starting materials - sand, bentonite, basalt glass, obsidian and two rhyolites. The duration of heating in the solar furnace, however, was limited due to the fact that the beam was horizontal, requiring a vertical orientation to the face of the sample thus allowing the melt to drop out of the hot zone as it formed. Consequently, only a small degree of fractionation was obtained. It was shown that the ratio of Fe^{2+} to Fe^{3+} increased with heating. No clear trend of silica fractionation could be determined from their results, but depletion of silica and alkalies and the concentration of alumina was noted.

Experiments on vapor fractionation in air by Walter and Carron (1964), using an induction furnace, were limited to 2100°C by the nature of the crucible material used (iridium). As in the solar furnace, only a small degree of fractionation was obtained. However, the results showed that the volatility of the alkalies was a function of the partial pressure of oxygen and that, at high oxygen pressures, the alkalies were not depleted.

The last, rather surprising, result is contrary to the intuitive expectation that alkalies would be boiled off from a high temperature melt. It also suggests that the compositional trends of individual tektite groups may be due to the process of vapor fractionation since, as the data of Barnes (1964) has shown, the alkali content of indochinites is relatively independent of the silica content. If such a process has, indeed, taken place, it should

then be possible to duplicate the compositional trends of tektites experimentally.

In order to accomplish these high-temperature experiments at atmospheric oxygen pressure, it was necessary to obtain the use of a large, vertically-oriented solar furnace. Dr. John Guitronich of the University of New South Wales collaborated in this phase of the research and the results of the study are published elsewhere in their entirety (Walter and Guitronich, 1967).

At the beginning of the investigation it was tacitly assumed that the starting composition could be represented by the low-silica end-member of the tektite compositional trends (ca. 65% SiO_2). However, O'Keefe (personal communication) suggested that the high-silica, Muong Nong type tektites might represent the unfractionated tektite parent material more closely because of the high degree of structure which they exhibit. These tektites are found in Indochina and were defined by Barnes (1961) as "layered" tektites. In thin section they show "shards" and cuspate voids which, as O'Keefe has suggested, should have been modified or destroyed by any substantial degree of heating. The discovery of coesite (Walter, 1965a), unstable at high temperatures and low pressures, in this type of tektite, provided proof that they had not been heated substantially after the time of formation of the coesite which, presumably, is the first stage of the formation of tektites as we see them. In all occurrences of coesite in tektites, the coesite is surrounded by frothy lechatelierite. Walter concluded that, while the frothing of the lechatelierite was indicative of a "moderate" degree of heating (about 1700°C or more), the retention of the coesite was an indication that this heating was momentary. Experimental investigations on coesite decomposition showed

that this mineral would break down to abundant cristobalite at moderate temperatures in a relatively short time (e.g., in 6 minutes at 1500°C). The lack of any indication of cristobalite in the X-ray patterns of tektite inclusions was indicative of a low degree of heating.

Dr. Barnes kindly permitted the author to inspect his collection of thin slices of Muong Nong specimens for the characteristic coesite-bearing inclusions. In figure 1, the occurrence of these inclusions is shown as a function of the index of refraction of the particular specimen. The results show that, with a high degree of probability, the coesite-bearing inclusions occur in specimens with low refractive index (i.e., high silica content). This is an indication that the high-silica Muong Nong type tektites are primary and presents the possibility that other, low-silica tektites may be derived from these.

In an earlier paper (Walter, 1965a), the pronounced homogeneity of a Muong Nong type tektite was pointed out. In that study, 100 randomly-selected points were analyzed by microprobe and the resulting distribution (shown here in figure 2, specimen PD2) had a strong peak. Examination of two sections of a coesite-bearing specimen from Kan Long Dong (figure 2, specimens KLD1C and KLD1F) do not exhibit such a uniform composition. This heterogeneity, however, does not contradict O'Keefe and Adler's (1966) contention that the Muong Nong type tektites could not consist of large, melted and partially homogenized mineral grains. They conclude that, because of the limitation on the degree of heating, the layered tektites have been originally made up of either minute crystals or glass fragments.

TEKTITE COMPOSITIONAL TRENDS

In order to compare the present experimental data with the trends in tektites, some suitable normalizing factor must be established. Normalization against SiO_2 content is used throughout this work for several reasons: (1) it develops that silica is one of the most volatile species in tektites; (2) it is more easily analyzed by microprobe than minor constituents; (3) as a major constituent, silica is always represented in tektite analyses and has been used by other workers for such normalization; (4) furthermore, it can easily be correlated with the index of refraction and density.

Another factor which should be examined is the effect of variation in a closed system. Since silica concentration is so high in tektites, independent variation in this component will be reflected in the concentrations of the other constituents. Meisch, Chao and Cuttitta (1966) have recently explored this complicating aspect of compositional trend analysis as it pertains to tektites. They found, as did Taylor (1962), that most elements are negatively correlated with SiO_2. It may be well, in the future, to apply these statistical methods to the experimental data presented here.

Tektite analyses have been compiled from the literature. The only analyses used were those published after 1957 when the availability of rock standards began, hopefully, to lead to more accurate analyses. The analyses used are comprised of those for 37 australites; 8 javanites; 32 philippinites; 33 indochinites; 44 moldavites and 35 North American tektites. Since, in general, the sources for these analyses are readily available (see Table 1), it is considered unnecessary to tabulate the data here.

Diagrams showing the relationship of the concentration of the major oxides to SiO_2 for the major groups comprising the australasian strewn field are shown in figures 3-6. The plots for moldavites and North American tektites are shown in figures 7 and 8.

The data in figures 3-8 have been fitted by two regression lines. The solid lines were determined by least squares perpendicular to the abscissa; the dashed lines by the same method parallel to the abscissa. The goodness of fit is apparent, in each case, by the degree of coincidence of these lines.

Of course, caution must be used in statistical derivation of a curve from a small number of points. This problem is apparent in the calcium distribution of the Javanites (fig. 4).

The data for the Ivory Coast tektites are not presented since only three old analyses are currently available. New data on a group of 14 Ivory Coast specimens (Chao et al., 1965) show a distribution from 67.2% to 69.1% SiO_2. This range is too limited to make the analyses of interest in this discussion. It should be pointed out, however, that since two of the three old analyses also fall within this range, the third, which contains 76.56% SiO_2 is rendered suspect.

In general, trends for Al_2O_3 and FeO_{total} (defined in the section on analyses) show a good correlation with SiO_2. The tightness of fit may be said to vary from excellent in the case of the North American group to good in the case of the moldavites. This may be a real difference, but it may be due, in part, to the fact that most analyses of North American tektites were performed in one laboratory. In addition to the close correlation with SiO_2 within each group, the slopes of the trends for these oxides are similar between the groups.

The correlation between K_2O and Na_2O and SiO_2 is good in the australites and indochinites and fair in the North American tektites. The compositional spread of the philippinites may not be sufficient to delineate a trend. In this case a negative correlation is indicated and it is strongly indicated

in the australites and indochinites. A negative correlation is also indicated by sodium in the North American tektites, but potassium in this group shows a positive slope.

The trend of magnesium may be regarded as a two- to three-fold concentration as silica decreases from 80% to 70%. This holds fairly well for the australites, indochinites, and philippinites (although the compositional range is smaller than in the first two groups). It also holds for the North American tektites since the magnesium content at about 80% SiO_2 is 0.5% or less. This results in a shallower slope.

The "anomolous" behavior of calcium has been pointed out by Schnetzler and Pinson (1964) and by Taylor (1966). The calcium vs. silica trend can, however, in some cases, be explained on the basis of two- to three-fold concentration factor over a 10% SiO_2 range. This holds for the indochinites and North American tektites and, perhaps, for the philippinites and moldavites. Philpotts and Pinson (1966) have pointed out that CaO varies at constant FeO in Bohemian moldavites and that FeO varies at constant CaO in Moravian moldavites. The two trends are not discernable in the CaO-SiO_2 relationships.

Two trends may be differentiated in the CaO-SiO_2 data for the australites. One group has a narrow range at about 70% SiO_2; the other extends from almost 80% to x70% SiO_2. These groups must conform to the two australite populations defined by Chapman, et al.(1964) on the basis of specific gravity. He compared the specimens from Manila Bay which were sharply defined and had a relatively high density (and, presumably, a lower silica content) to philippinites. Indeed, the CaO-SiO_2 distribution for the narrow-ranged australite (fig. 3) group is similar to the philippinite distribution (fig. 5). On the other hand, specimens from southwest Australia were found to have generally lower and

broader distribution of density (indicating, on the whole, higher silica content). This group would be represented in figure 3 by those analyses which show a broader silica distribution. The two CaO-SiO_2 groups in this figure independently define trends which are similar to those in the indochinites and North American tektites. The regression lines in figure 3 (CaO) were calculated using all the points shown. If two trends exist, they can be explained on the basis of heterogeneity of the starting material which has been shown to exist in Muong Nong type tektites. The starting materials for the two trends cannot be specified but, since the double trend is not obvious in any of the other distributions, it is tempting to suggest a variation in only the calcium content. Thus the addition of 1.5% CaO to a parent material of the "defined" group containing approximately 82% SiO_2 and 0.5% CaO would produce the starting material (80% SiO_2, 2.0% CaO) of the "broad" group. This independent variation of CaO has been suggested by Schnetzler and Pinson (1964).

The strong and consistent variation of Al_2O_3 and FeO with SiO_2 must be explained on the basis of some systematic process. Philpotts and Pinson (1966) have presented some cogent arguments against either the mixing of sedimentary rocks or an igneous fractional crystallization process as the cause of the compositional relationships. The results of a computer analysis of 4876 of Washington's (1917) superior analyses of igneous rocks are shown in figure 9. The curves show the mean distribution of Al_2O_3, K_2O and MgO versus SiO_2. The significance of the curves is that, for rocks with a silica content indicated on the abscissa, half have oxide contents higher and half lower than the value indicated by the curve on the ordinate. While the Al_2O_3-SiO_2 relationship is similar to that found in tektites, the relationships between

SiO_2-MgO and SiO_2-K_2O (at least below 75% SiO_2) are unlike that found in tektites. While a very strong case cannot be based on these "median" trends, these data, combined with the arguments by Philpotts and Pinson, present a strong case against a crystal fractionation process.

EXPERIMENTAL

The analytical results on tektites in the previous section are to be compared with the experimental results of studies by Walter and Guitronich (1967) which are presented in figure 10. These data are the results of high-temperature vapor fractionation experiments performed in air atmosphere in a solar furnace on a synthetic glass of the composition represented by the high-silica (ca. 82%) end-points of the fractionation curves. The conditions of the runs are presented in Table 2. The analyses were performed by microprobe; therefore, iron is reported as FeO and the errors for the lighter elements (sodium and magnesium) are rather large. The curves shown are derived by the least-squares analysis of the microprobe data. Some other aspects of the microprobe analytical techniques are discussed in Appendix 1.

The data used to determine one of the curves shown in figure 10 are illustrated in figure 11. It is obvious in this figure that many of the analyses are grouped at the high and the low ends of the fractionation curve although many points occur along the curve. These intermediate values come from a relatively narrow (ca. 300 micron) region of the approximately 2 cm. sample. Thus, although a strong thermal gradient exists in a sample in a solar furnace, it appears that convection in the silicate melt was sufficient to homogenize the fractionating material down to the level at which the melt started to flow. In between the homogenized melt and the solid starting material was a narrow

region in which the materials were partially mixed. Points along the curve, therefore, do not represent the fractionation trend, per se, but, rather the mixing of the two (fractionated and unfractionated) materials. Although the starting material does not necessarily fractionate along the curve defined by the points, the trend is certainly toward the low-silica end-member and probably follows fairly closely to the linear relationship shown.

In other runs in which the degree of fractionation is small (cf, runs 7 and 9) compositional changes in the major oxides were insufficient to define a trend. Therefore, in some of these runs, the fractionation curves can differ markedly from those in which a higher degree of fractionation was attained.

The same starting material was used in vapor fractionation experiments in which the melt was heated in a tungsten crucible by an induction furnace. The crucible, about ¼ inch in diameter and 3/16 inch deep, was heated in a ten-kilowatt induction furnace while under about 10^{-3} mm_{Hg} pressure of air. The conditions of the runs are given in Table 3.

Results of the microprobe analysis of the material which was heated in tungsten are illustrated in figure 12. Because iron was probably absorbed into the tungsten during the run, its depletion in the residuum cannot be considered significant although loss of iron by this mechanism results in a small, anomolous increase in the abundance of the other components. Other components should not be affected directly by the tungsten except insofar as the presence of tungsten lowers the oxygen pressure.

The results of vapor fractionation under these reducing conditions are, in other respects, markedly different from those under oxidizing conditions. The most notable difference is in the behavior of alkalies which decrease

strongly with only a small decrease in silica content. Another notable difference is the steeper slope of the alumina fractionation curve.

Unfortunately the starting composition differs from the Muong Nong type composition in several respects. The calcium content is low by a factor of two, being .51% in the experimental starting material. As previously discussed, the experimental curve for CaO is thus less steep than if the starting material had been in the 1% range.

Another, and probably more serious, difference is in the potassium content which is approximately 1% in the experimental starting material and 2% in the Muong Nong type tektites. It is entirely conceivable that, with higher potassium content, the rate of loss might be greatly increased. In order to check this, another experiment, using a different starting material with a higher potassium content, was performed and the results are shown in figure 13. In this case, the glass was placed in the hot zone of an arc welder. Temperatures attained were in the range of 3000°C, and fractionation was extreme, although the time of heating was only about one minute. The ambient was one atmosphere of air and the results, as far as potassium is concerned, are similar to those obtained for the lower potassium starting material used in the solar furnace experiments.

CONCLUSIONS

A comparison between the results of the vapor fractionation experiments and the compositional trends in tektites seems to indicate that these trends are the result of a vapor fractionation process which took place at relatively high oxygen pressures. Some objections to this conclusion, however, may be anticipated.

(1) Discrete inclusions of lechatelierite occur in tektites throughout their compositional range. If tektites have originated through a high-temperature fractionation process, a logical question is whether the lechatelierite grains

would not have been dissolved during this process. Experiments carried out by Joseph Bishop of the Planetology Branch have demonstrated the presence of lechatelierite inclusions in silicate glasses despite extensive vapor fractionation. In this work, finely crushed silica glass was mixed with powdered glass of the composition used in the solar furnace runs. These were exposed to high (3000°C) temperatures in an induction heater using graphite as a susceptor and crucible. Under these conditions, approximately two-thirds of the sample (visual estimation) was boiled away in about three minutes. Nevertheless, microscopic examination of these samples showed that discrete lechetelierite particles still remained. It thus seems possible that the parent tektite material could have undergone high temperature vapor fractionation while preserving discrete lechetelierite fragments.

(2) Another problem concerns the time required for vapor fractionation to cover the range of tektite compositions. According to table 2 and figure 10, vapor fractionation under oxidizing conditions results in a decrease in the silica content from 82 to approximately 75% in about 5-10 minutes at 2800°C. It is hard to imagine that high-temperature conditions could be sustained this long either through the parent body or meteorite impact hypotheses. However, since runs of this duration at 2200°C (Walter and Carron, 1964) produced little change in the silica content, it is quite likely that the volatilization rate varies strongly with temperature. Consequently, it seems likely that an increase in the temperature to over 3000°C would be sufficient to cause fractionation over the entire tektite range in periods of less than one minute. Lovering (1960) has previously discussed this aspect of the problem of vapor fractionation and proposed that temperatures in the order of 10,000°C were attainable, thus almost obviating the problem. It seems likely from the experimental results that such enormous temperatures are not required.

(3) If the experimental data obtained under oxidizing conditions are to be used, a question arises as to the oxidation state of the iron in the glass produced under these conditions in comparison with the very low Fe^{2+}/Fe^{3+} ratio found in tektites. Cohen (1962) has previously suggested that, with increasing temperature, the Fe^{2+}/Fe^{3+} ratio should increase. His suggestion was based on the general tendency of such systems to undergo reduction at constant P_{O_2} with increasing temperature. This effect was noted in the experimental work of Friedman et al. (1960). More recently, Johnson (1964) has reported the results of experiments on silicate glasses in which the process was also noted. Although the ratio was not lowered to that observed in tektites, the temperatures attained in his experiments ($1400^{o}C$) were not nearly so high as those proposed for the volatilization mechanism. Another possibility is that the parent tektite material had an initially low ferric-ferrous ratio and that, at the free surface, material was, indeed, oxidized while being volatilized in the atmosphere. The interior, in this case, might not become oxidized since mass transfer during this process would be from the inside towards the outside of the tektite. In either case, the ferric-ferrous ratios observed in tektites do not seem to impose any insurmountable obstacle in the consideration of vapor fractionation under oxidizing conditions.

(4) Although experimental volatilization under oxidizing conditions (figs. 10 and 11) show that sodium is concentrated in the residuum, analyses of australites (Taylor, 1961) have indicated that sodium is depleted in the flanges. These analyses have been corroberated by Cobb (1967). This work indicates a small depletion of sodium in the flange, but this is coupled with a significant depletion in chromium which is considered refractory. The author concludes, therefore, that the question of fractional volatilization during the process of australite flange formation is problematical.

(5) While the tektite analytical data usually indicate a negative correlation between potash and silica, the experimental results show a slight positive correlation. Of the K_2O-SiO_2 correlations shown in figs. 3-8, those of the javanites, philippinites and moldavites are either based on too few points or show too much spread to enable any firm conclusions regarding the trends. In the australites, the true trend is probably obscured by the fact that we are dealing with two distinct groups. The "defined," low-silica group has a significantly higher K_2O-content. The "broad" group which, as mentioned, exhibits a good CaO-SiO_2 correlation, exhibits a horizontal or slightly positive K_2O-SiO_2 relationship. The negative correlation in the indochinites is very slight and based strongly on three analyses at high SiO_2-content. The correlation for the North American tektites agrees with the results of experimental work.

Although the K_2O-SiO_2 correlation in the experimental run product shown in fig. 10 is positive, the results cover a broad range of silica contents. Often, trends which cover a narrower range of SiO_2 values (fig. 9) will deviate from this trend either because of sampling or analytical error. It would seem that the experimental results, over the tektite compositional range, indicate an ostensibly horizontal K_2O-SiO_2 correlation as shown in fig. 12 and that this is in fairly good agreement with those tektite groups for which there are sufficient and broad (in terms of SiO_2 values) analyses. The fact that one curve may be slightly positive or negative is unimportant since this only means that the volatility of the species is slightly more or less than SiO_2. It is doubtful whether the data are sufficiently good to permit this distinction.

Microprobe analyses of Ca, Si and Al in two australites have shown that the compositional difference between the flange and the core is certainly much less than the compositional fluctuations in the flange or the core. The results for one of the two australites examined are shown in figure 14 and the analysis of the data is given in table 4. The results for the other australite were similar. The compositional difference between the flange and the core is obviously well within the analytical error. The spread of the analyses, as indicated by the standard deviation from the mean, shows that any differences must be less than the heterogeneity of the australite glass itself. Since, according to the experimental vapor fractionation results, these elements are most sensitive to this process, it is concluded that the effects of vapor fractionation during australite flange formation are minimal. Thus, while some fractionation must have occurred during the formation of the australite flanges (Walter and Adams, 1967), the extent of this process was not so severe as that which resulted in the tektite compositional trend. The temperature and/or time of formation of the flanges may not have been as extreme and the material may have flowed away from the stagnation point

in relatively thick layers which were heated to extreme temperatures to only a very small depth.

It does not seem likely that any of the data obviates the possibility of vapor fractionation as the cause of tektite compositional trends. Comparison between these trends and those for the experimental results under oxidizing conditions shows a striking similarity. The simple compositional relationships of Al and Fe with Si in tektites probably have a simple explanation. It would seem that vapor fractionation does explain these trends and, at the same time, ties in with the observation of coesite in the high-silica, highly structured Muong Nong type tektites.

Vapor fractionation also explains the relationship between oxygen isotopic composition and silica content discovered in the bediasites by Taylor and Epstein (1962). More recently, Garlick (1966) has shown that fractional crystallization processes produce a direct correlation between O^{18}/O^{16} and a parameter which he terms "chemical index." All sequences of igneous rocks examined exhibit such a direct correlation but the bediasites correlate inversely. In a study by Walter and Clayton (1967) the O^{18}/O^{16} ratio of the product of run #4 (fig. 12) was compared with that of the starting material. The results showed a significant increase in this ratio with decreasing silica content as in the case of the bediasites.

The most significant result of a study of tektites would be the determination of their origin. Unfortunately, this is impossible since the high temperatures necessary for differential volatilization could be obtained either through meteoritic impact or during the ablation of a parent body.

Two conclusions, however, are of some importance. First, in at least three of the four known strewn fields, the tektites were derived from a single

parent material and this material contained at least 82% silica. It should be emphasized that the australite analyses indicate that this parent material was somewhat heterogeneous with respect to CaO. Second, this vapor fractionation process could not have taken place under reducing conditions since, as shown by the runs produced in the tungsten crucibles, vapor fractionation under reducing conditions results in a severe loss of alkalies. In addition, the relationship between alumina and silica is quite dissimilar from that which occurs when fractionation takes place under oxidizing conditions. It follows from this that the extreme heating of tektites which resulted in their vapor fractionation took place near the earth's surface under moderate oxygen pressure. This, it seems, rules out the hypothesis of a direct entry from the moon for the origin of tektites.

DISCUSSION

Recent studies by Schnetzler, Hurley and Pinson (1966); Schnetzler, Philpotts and Thomas (1966) and Taylor and Epstein (1966), have closely correlated the rocks at the Bosumtwi Crater (Ghana) with the Ivory Coast tektites, thus lending strong support to a terrestrial origin. On the other hand, many of the arguments against this origin, such as the requirement of blasting tektites through or along with the atmosphere (O'Keefe, 1966), are still viable. Neither this evidence or that presented in this paper can permit this author to decide, with any certainty, between a terrestrial and a lunar origin for tektites.

This work, however, gives some support to a lunar origin because it is difficult to ascribe the four tektite groups to four different terrestrial impact sites which had material with at least 82% silica. (The Ivory Coast

tektites may have had a lower silica starting material, but three areas still remain which must have had this high-silica material.) It might be pointed out that of the impact and possible impact glasses which are reported by Chao (1963), all but the glass from the Ries Crater are exceptionally high in silica. Since the other craters (Wabar, Henbury and Aouelloul) discussed by Chao occur in sedimentary rock, it might be concluded that there is a high probability that a large meteorite striking the earth will strike a high-silica material. (The Ries material indicates that glass formation does not require a silica content of 80%.) It is more likely, however, that craters in highly siliceous material will last longer and will be detected more easily. Thus, the rather poor statistics might have a simple explanation. Because of our relative lack of knowledge about the composition of the lunar surface, one can arbitrarily postulate high-silica surface material, but this seems to be a Deus ex machina. Some evidence for such a material exists, however (O'Keefe and Cameron, 1962), and Walter (1965b) has proposed some mechanisms by which magmatic differentiation under lunar conditions might result in residua which would be more siliceous than their terrestrial counterparts. This work, while speculative, was produced a priori to the requirement for a high-silica starting material. It indicates several reasons why the residual magmas arriving at the lunar surface would be close to the maximum silica content of 75-80%. Since such magmatic residua contain about 10% total alkalies and since these would boil off if the magma were exposed to vacuum at the lunar surface, the silica content could be raised to the 80-82% level required for the tektite parent material.

Appendix 1

Analytical Techniques

The method of microprobe analysis used in this work involved direct interpolation (and limited extrapolation) using homogeneous synthetic glass standards of tektite composition; $SiO_{2\,quartz}$ and α-Al_2O_3 as standards. The counts for standards and samples were normalized against constant integrated sample current. This current, caused by the absorbtion of electrons in the sample under analysis, was stored in a precision capacitance-type current integrater which triggers the printout cycle when a preset number of coulombs is attained. Ordinarily, it would be difficult to use these data if correction procedures were to be used since such procedures are based on constant integrated beam current being held constant between samples. However, in the present work, the data are employed only in interpolation between standards; since the matrices of standards and samples are similar, normalized sample current is possible. However, beam current sampling and normalization could, of course, be used if the data are to be interpreted by interpolation. The integration method has two advantages: 1) it helps greatly in smoothing out the effects of short-time instability in the power supplies of the microprobe and 2) it is essential in the techniques used here for the analysis of sodium.

It is well-known that sodium volatilizes readily from glasses during microprobe analysis. In developing a technique for sodium analysis, several methods were attempted. The one which gave the highest precision was the use of a fairly intense beam (20 KV and .05 μa) for only about 10 seconds. This method produces only about 500 total counts for Na at the 1% concentration level, but after 10 seconds the count rate is relatively independent of the initial sodium concentration since so much sodium has been boiled off. The technique

hinges on the ability to begin integrating X-ray counts at the moment the electron beam hits the sample so that the volatilization is kept constant. It may be of interest to note that potassium which is more volatile than sodium in the vaporization experiments, is not subject to vaporization during microprobe analysis. The loss of sodium is apparently the result of the breaking of chemical bonds because of the presence of excess electrons rather than because of an increase in temperature. (The high temperatures required to "boil off" alkalies in the microprobe should result in an intense glow which certainly is not apparent during analysis.)

Since the microprobe cannot differentiate ferric and ferrous iron, all results in this paper are presented in terms of FeO_{total}. In obtaining this value for standards and for the results of wet chemical analyses, Fe_2O_3 was recalculated to FeO and added to the balance of the FeO in the analysis. This conversion has little effect on the tektite analyses because of their low ferric iron values. Ferric iron was not determined in the experimental run products.

Accumulated counts for standards and samples were punched onto paper tape and the information transferred to punched cards. A computer was used to fit linear and quadratic equations to the data for the standards which were run before and after a given set of samples. It then evaluated the sample data, adjusting the equations to vary linearly between the first and second sets of standards. This represents another attempt to soften the effect of machine drift and, since standards were run every fifteen or twenty minutes, it was effective. The output of the computer run was automatically placed on punched cards to facilitate the computation of the least-squares relationships of the oxides to silica.

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Figure Legends

1. Occurrence of coesite-bearing inclusions in 22 Muong Nong type tektites as a function of refractive index. The refractive index scale has been converted to an SiO_2 scale (above) using the relationship of Chao (1963). The specimens were from the collection of Dr. Virgil Barnes who determined the refractive indices.
2. Distribution of microprobe analyses of randomly-selected points in Muong Nong type tektites from Phaeng Dang (PD) and Kan Long Dong (KLD). Two separate sections of the KLD specimen were examined.
3. Major oxide-silica correlations for australites showing regression lines (see text). FeO_{total} is defined in Appendix 1.
4. Major oxide-silica correlations for javanites.
5. Major oxide-silica correlations for philippinites.
6. Major oxide-silica correlations for indochinites.
7. Major oxide-silica correlations for moldavites.
8. Major oxide-silica correlation for North American tektites.
9. Correlation of Al_2O_3, K_2O and MgO with SiO_2 for 4876 superior igneous rock analyses. See text for explanation of the derivation of the curves.
10. Results of vapor fractionation experiments by Walter and Guitronich (1967). See Table 2 for run conditions. Curves are obtained by minimizing the squares of the deviations taken perpendicular to the abscissa. Curve "C" was derived by combining the data in Runs 9, 10 and 11.
11. Data points of Run #4 (Walter and Giutronich, 1967).
12. Results of vapor fractionation at low oxygen pressures in tungsten crucibles. Run conditions are given in Table 3. Curves shown are not fit statistically.

Figure Legends (continued)

13. Results of vapor fractionation experiment using material with higher K_2O content. Experiment was performed using an electric arc welder at one atmosphere pressure. Composition of starting material is marked by "X."

14. Distribution of CaO, SiO_2 and Al_2O_3 microprobe analyses for randomly selected points in the core and flange of one australite. Mean values are indicated by "M." See Table 4.

Table 1

References for Analyses Used in Figures 3-9

Number of Analyses	Reference	Ref. Type[1]
Australasian Tektites		
Australites		
22	Schnetzler and Pinson, 1963	4P, 18S
15	Taylor and Sachs, 1964	P
Javanites		
2	Schnetzler and Pinson, 1963	P
6	Cuttitta et al., 1964a	P
Philippinites		
4	Cuttitta et al., 1962	P
15	Schnetzler and Pinson, 1963	S
13	Cuttitta et al., 1964b	P
Indochinites		
12	Schnetzler and Pinson, 1963	S
5	Cuttitta et al., 1964b	P
16	Barnes, 1964	P
Moldavites		
6	Schnetzler and Pinson, 1964	P
1	Schnetzler and Pinson, 1963	P
14	v. Engelhardt and Hörz, 1965	S
23	Philpotts and Pinson, 1966	P
North American		
19	Chao, 1963	P
5	Schnetzler and Pinson, 1963	S

Table 1 (continued)

Number of Analyses	Reference	Ref. Type[1]
North American		
8	Cuttitta et al., 1966	P
3	King, 1966	P

[1]"Type" refers to whether the reference is primary (P) or secondary (S).

Table 2

Conditions of Runs Shown in Figure 10

Run No.	Temp. (°C)	Duration (mm.)	Lowest Silica Content Measured
4	2800	45	45
7	2600-2700	13	72
8	2800	13	74
9	2700	5	78
10	> 2800	10	70
11	2800	10	
	2600	5	70
C	Composite of runs 9, 10 and 11		

Table 3

Conditions for Runs in Tungsten Crucibles Shown in Figure 12

(All runs at 10^{-3} mm_{Hg} pressure)

Sample	Temperature (^{o}C)	Duration (mm)
418	2300	15
419	2700	1
420	2700	5
421	2700	1
424	2700	3

Table 4

Results of Analysis of Australite

	CaO	SiO_2	Al_2O_3
Flange mean (%)	4.6_3	$74._1$	13.9_4
abs. σ	.31	.72	.35
Core mean (%)	4.6_8	$74._4$	13.9_5
abs. σ	.23	.83	.28
Estimated precision of microprobe analysis (abs. %) at 95% confidence level	.05	.5	.2

REFERENCES

Barnes, Virgil E., 1961, A world-wide geological investigation of tektites, Geotimes 6, no. 2, pp. 8-12, p. 38.

Barnes, Virgil E., 1964, Variation of petrographic and chemical characteristics of indochinite tektites within their strewn fields, Geochim. et Cosmochim. Acta 28, pp. 893-913.

Chapman, Dean R., Howard K. Larson and Leroy C. Scheiber, 1964, Population polygons of tektite specific gravity for various localities in Australasia, Journal of Geophysical Research 28, pp. 821-839.

Chao, E. C. T., 1963, The petrographic and chemical characteristics of tektites, in Tektites, ed. by John A. O'Keefe, U. of Chicago Press, Chicago, Ill., pp. 51-94.

Clarke, Roy S., Jr. and John F. Wosinski, 1967, Baddelyite inclusion in the Martha's Vineyard tektite, Geochim. et Cosmochim. Acta 31, pp. 397-406.

Cobb, James C., 1967, A trace element study of tektites, submitted to Geochim. et Cosmochim. Acta.

Cohen, Alvin J., 1960, Trace element relationships and terrestrial origin of tektites, Nature 188, pp. 653-654.

Cuttitta, Frank; M. K. Carron, J. D. Fletcher and E. C. T. Chao, 1962, Chemical composition of bediasites and philippinites, U. S. Geological Survey, Astrogeologic Studies, Semi-annual Progress Report, Feb. 26, 1961 to Aug. 24, 1961, pp. 15-47.

Cuttitta, Frank; E. C. T. Chao, M. K. Carron, J. Littler, J. D. Fletcher and C. Annell, 1964a, Some physical properties and the chemical composition of Australite tektites, U. S. Geological Survey, Astrogeologic Studies Annual Progress Report, Aug. 25, 1962 to July 1, 1963, Part C, pp. 1-52.

Cuttitta, Frank; E. C. T. Chao and M. K. Carron, 1964b, The chemical composition of selected indochinites and philippinites, U. S. Geological Survey, Annual Progress Report, July 1, 1963 to July 1, 1964, Part C.

Cuttitta, F., R. S. Clarke, Jr., M. K. Carron and C. S. Annell, 1966, Martha's Vineyard and selected Georgia tektites: new chemical data , Astrogeologic Studies: Annual Progress Report, '65-'66, Part C, Cosmic Chemistry and Petrology.

Friedman, I., Arthur Thorpe and F. E. Senftle, 1960, Comparison of the chemical composition and magnetic properties of tektites and glasses formed by fusion of terrestrial rocks, Nature 187, pp. 1089-1092.

Garlick, G. O., 1966, Oxygen isotope fractionation in igneous rocks, Earth and Planetary Science Letters 1, pp. 361-368.

Johnston, W. D., 1964, Oxidation-reduction equilibria in iron-containing glass, Jour. Am. Ceramic Soc. 47, pp. 198-201.

King, Elbert I., 1966, Major element composition of Georgia tektites, Nature 210, pp. 828-829.

Lovering, J. F., 1960, High-temperature fusion of possible parent materials for tektites, Nature 186, pp. 1028-1030.

Meisch, A. T., E. C. T. Chao and F. Cuttitta, 1966, Multivariant analysis of geochemical data on Texas tektites (bediasites), Jour. Geology , pp. 673-691.

O'Keefe, J. A. and Cameron, W. S., 1962, Evidence from the moon's surface for the production of lunar granites," Space Research III, Proc. of the Third International Space Sciences Symposium, Washington, D. C., April 20-May 9, 1962, ed. by W. Priester, Amsterdam, Holland (North-Holland Publishing Co.); also published in Icarus 1, 271-285 (1962).

O'Keefe, John A., 1966, The origin of tektites, Space Science Reviews 6, pp. 174-221.

Philpotts, J. A. and Pinson, W. H., Jr., 1966, New data on the chemical composition and origin of moldavites, Geochim. et Cosmochim. Acta 30, pp. 253-266.

Schnetzler, C. C. and W. H. Pinson, Jr., 1963, The chemical composition of tektites, pp. 95-129, in Tektites, J. A. O'Keefe, ed., U. of Chivago Press, Chicago, Ill.

Schnetzler, C. C. and W. H. Pinson, Jr., 1964, A report on some recent major element analyses of tektites, Geochim. et Cosmochim. Acta 28, 793-806.

Schnetzler, C. C.; P. M. Hurley and W. H. Pinson, Jr., 1966, Rubidium-strontium age of the Bosumtwi crater area, Ghana, compared with the age of the Ivory Coast tektites, Science 151, pp. 817-819.

Schnetzler, C. C., John A. Philpotts and H. H. Thomas, Rare-earth and barium abundances in Ivory Coast tektites and rocks from the Bosumtwi crater area, Ghana, submitted to Geochim. et Cosmochim. Acta.

Taylor, Hugh P., Jr. and Samuel Epstein, 1962, Oxygen isotope studies on the origin of tektites, J. Geophys. Res. 67, pp. 4485-4490.

Taylor, Hugh P., Jr. and Samuel Epstein, 1966, Oxygen isotope studies of Ivory Coast tektites and impactite glasses from the Bosumtwi crater, Ghana, Science 153, pp. 173-175.

Taylor, S. R., 1961, Distillation of alkali elements during formation of australite flanges, Nature 189, pp. 630-633.

Taylor, S. R., 1962, The chemical composition of australites, Geochim. et Cosmochim. Acta 26, pp. 685-722.

Taylor, S. R. and Maureen Sachs, 1964, Geochemical evidence for the origin of australites, Geochim. et Cosmochim. Acta 28, pp. 235-264.

Taylor, S. R., 1966, Australites, Henbury impact glass and subgreywacke: a comparison of the abundances of 51 elements, Geochimica et Cosmochimica Acta 30, pp. 1121-1136.

von Engelhardt, W. and F. Hörz, 1965, Riesglaser und Moldavite, Geochim. et Cosmochim. Acta 29, pp. 609-620.

Taylor, Hugh P., Jr. and Samuel Epstein, 1964, Comparison of oxygen isotope analyses of tektites, soils and impact glasses, Ch. 14 of Isotopic and Cosmic Chemistry, ed. by H. Craig, S. L. Miller and G. J. Wassenberg, N. Holland Publishing Co., Amsterdam.

Walter, L. S. and M. K. Carron, 1964, Vapor pressure and vapor fractionation of silicate melts of tektite composition, Geochim. et Cosmochim. Acta 28, 937-951.

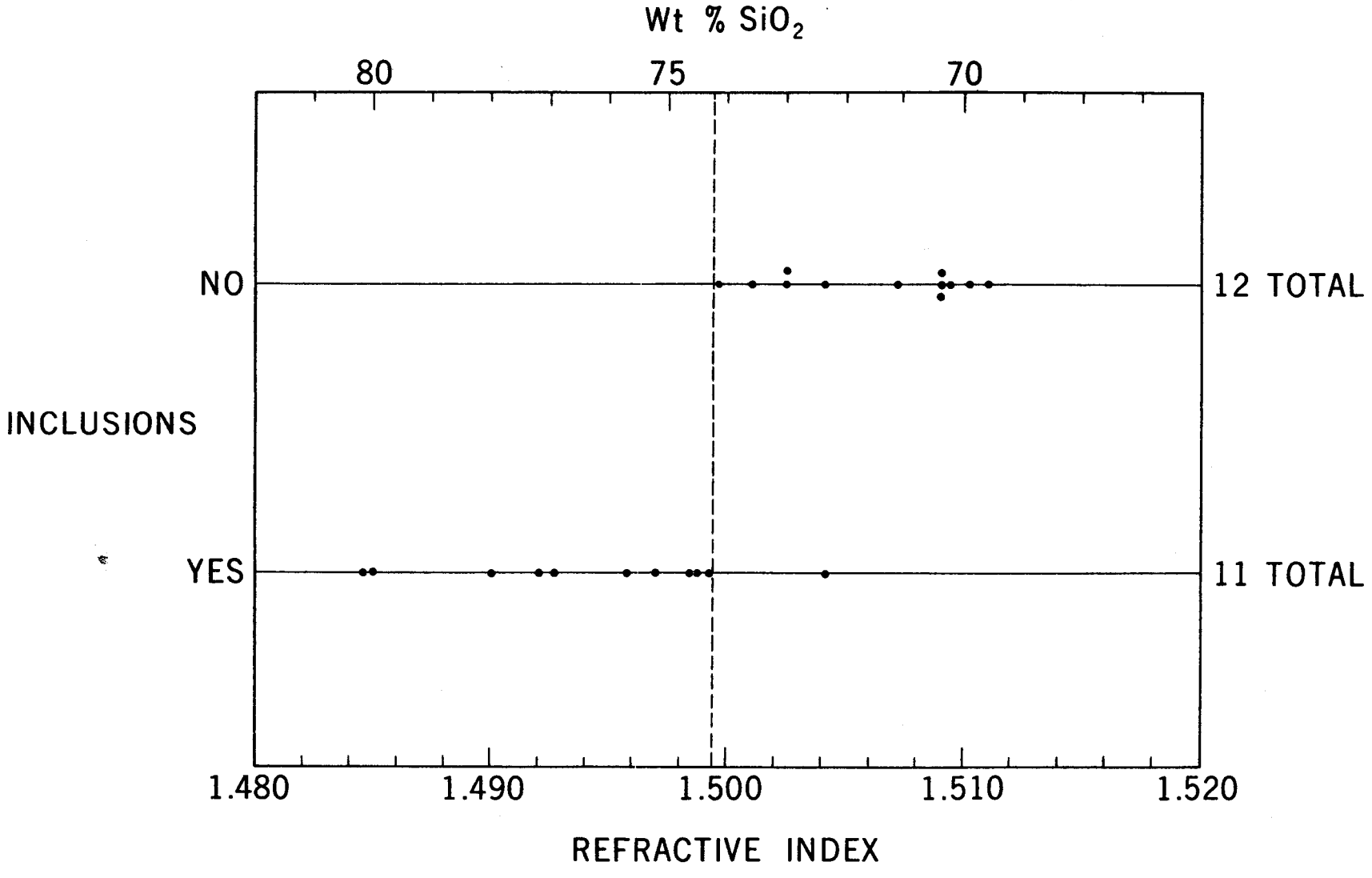
Walter, L. S., 1965a, Coesite discovered in tektites, Science 147, pp. 1029-1032.

Walter, L. S., 1965b, Lunar differentiation processes, New York Acad. Sci. Annals 123, pp. 470-480.

Walter, L. S. and Giutronich, J. F., 1967, Vapor fractionation of silicate melts at high temperatures and atmospheric pressure, in press, Solar Energy Journal.

Walter, Louis S. and Robert N. Clayton, 1967, Oxygen Isotopes: Experimental vapor fractionation and variations in tektites, Science, in press.

Washington, H. S., 1917, Chem. analysis of igneous rocks, U. S. G. S. Prof. Paper 99, Washington, D. C.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75
70
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INCLUSIONS
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11 TOTAL
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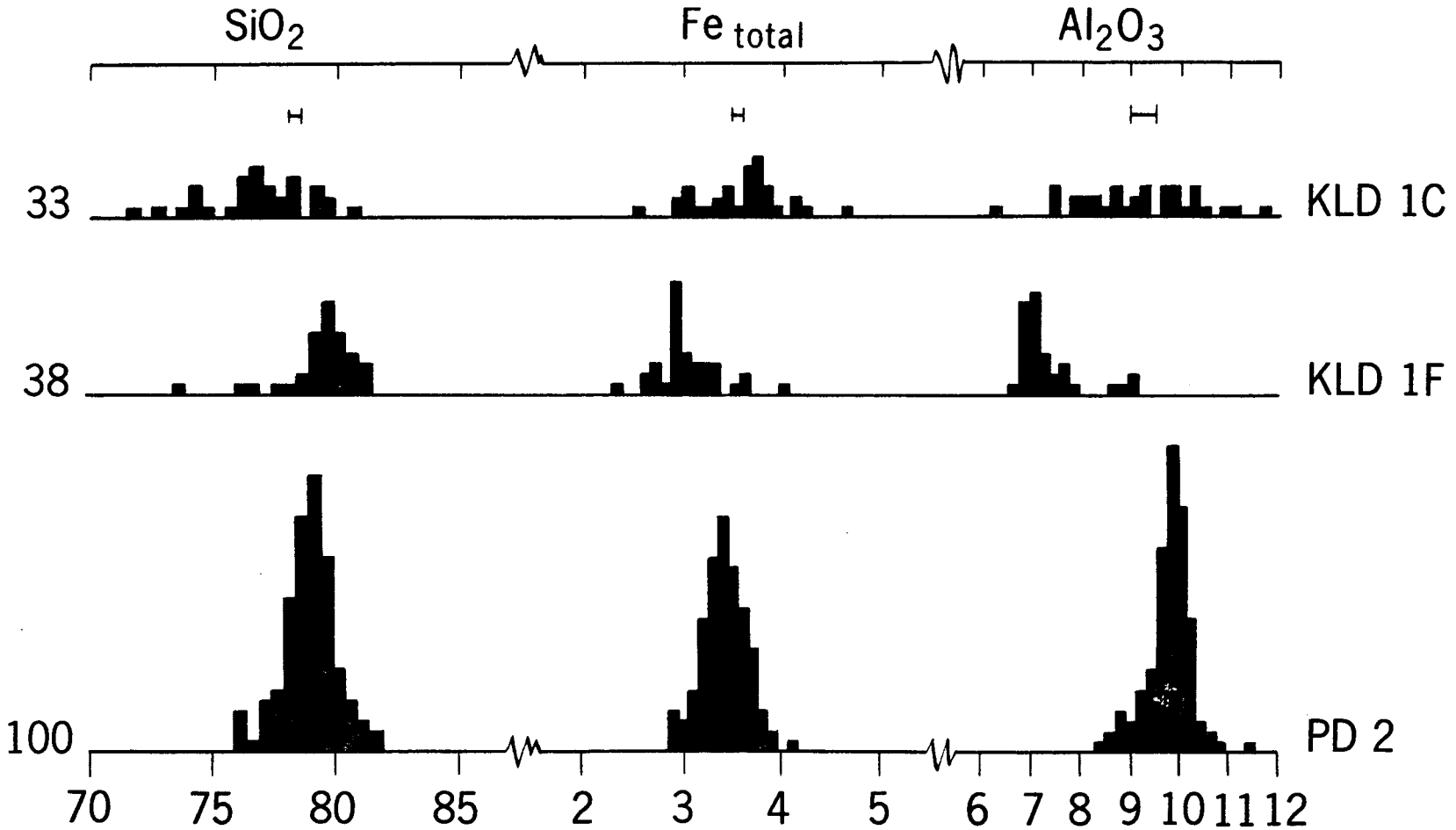
1.520
REFRACTIVE INDEX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Fe total
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KLD 1C
38
KLD 1F
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PD 2
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75
80
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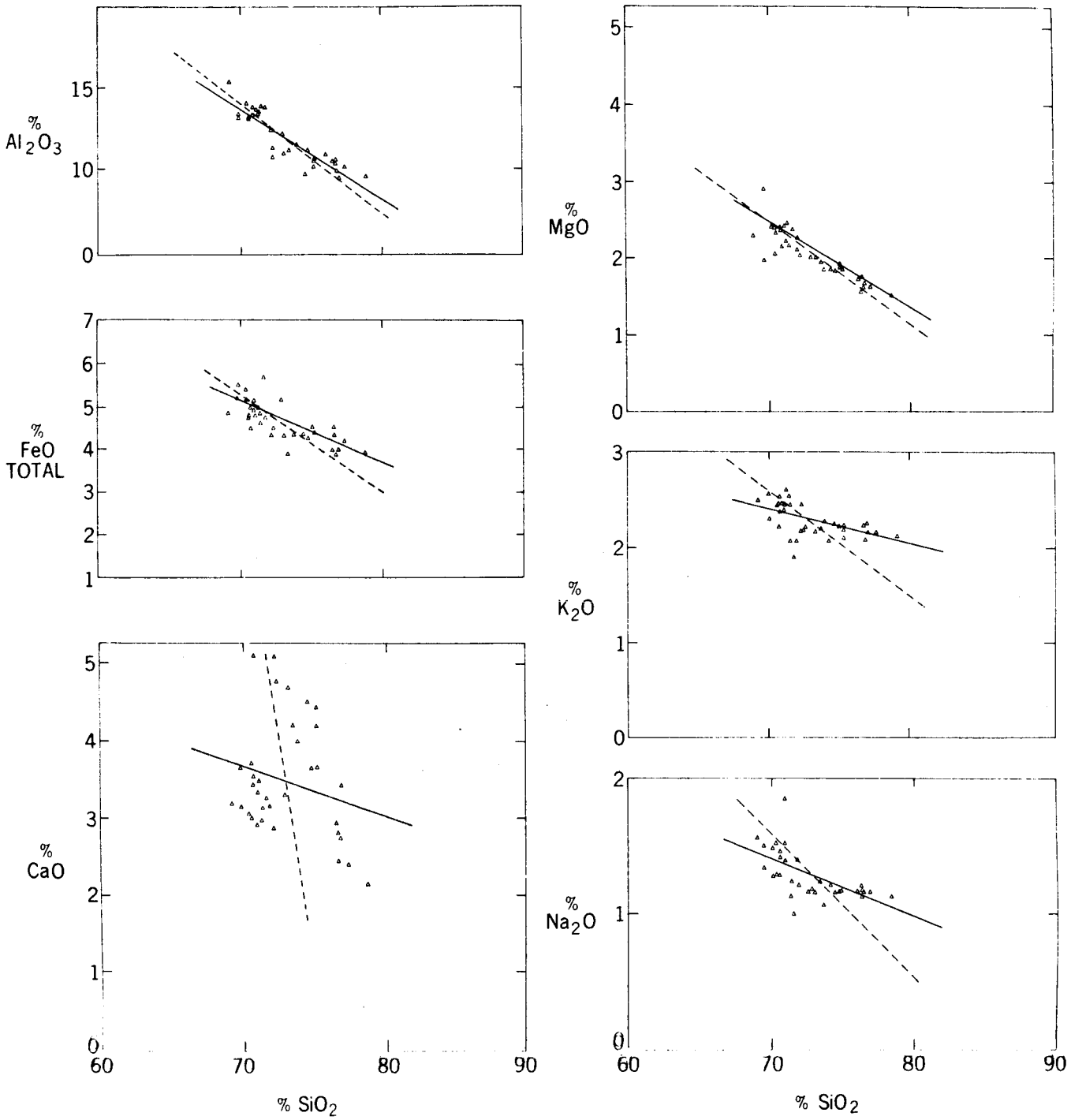
2
3
4
5
6
7
8
9
10
11
12

AUSTRALITES



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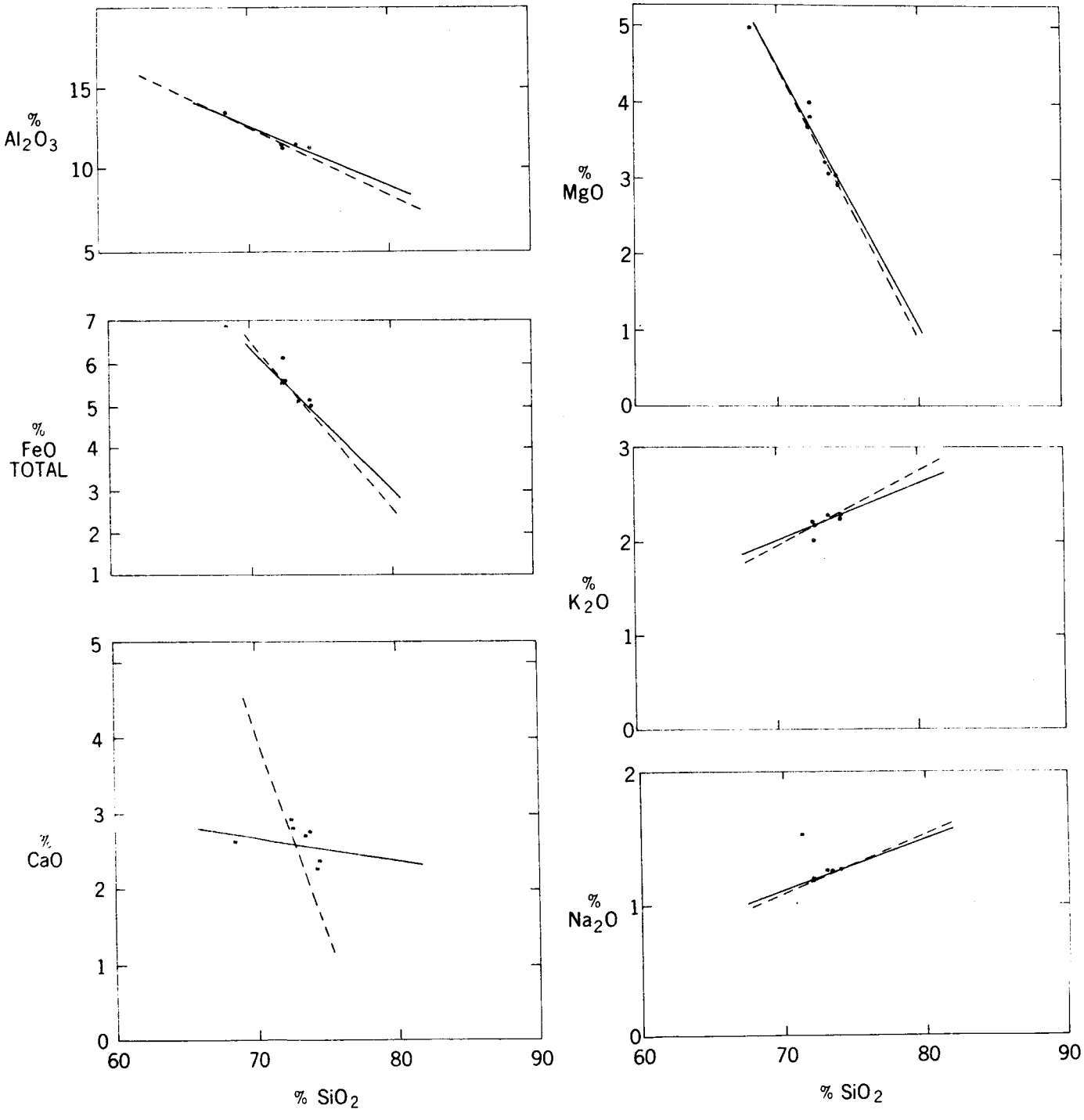
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5
% MgO
5
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0
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4
3
2
1
% K_2O
3
2
1
0
% CaO
5
4
3
2
1
0
% Na_2O
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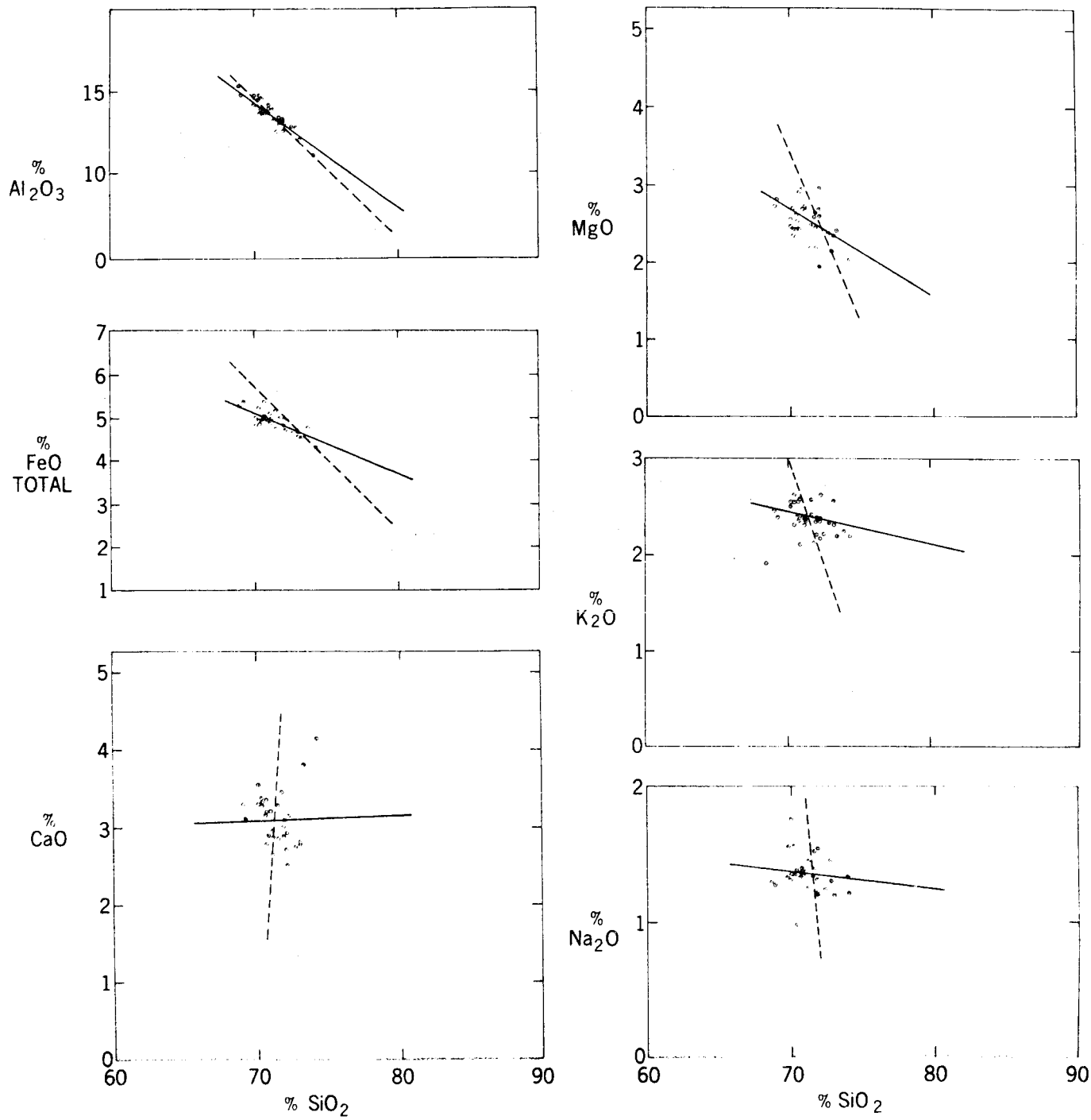
80
90
% SiO_2
60
70
80
90
% SiO_2

PHILIPPINITES



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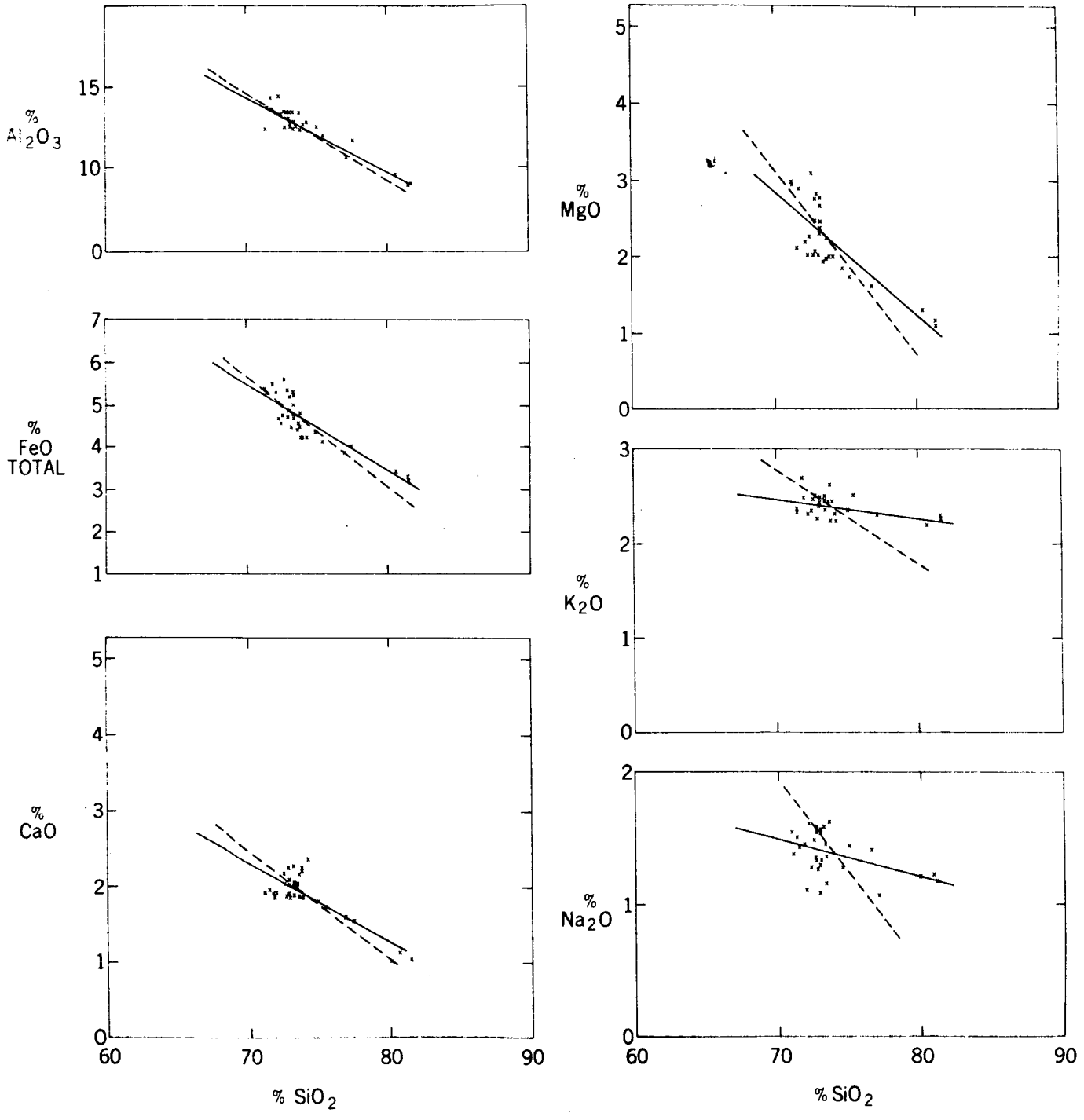

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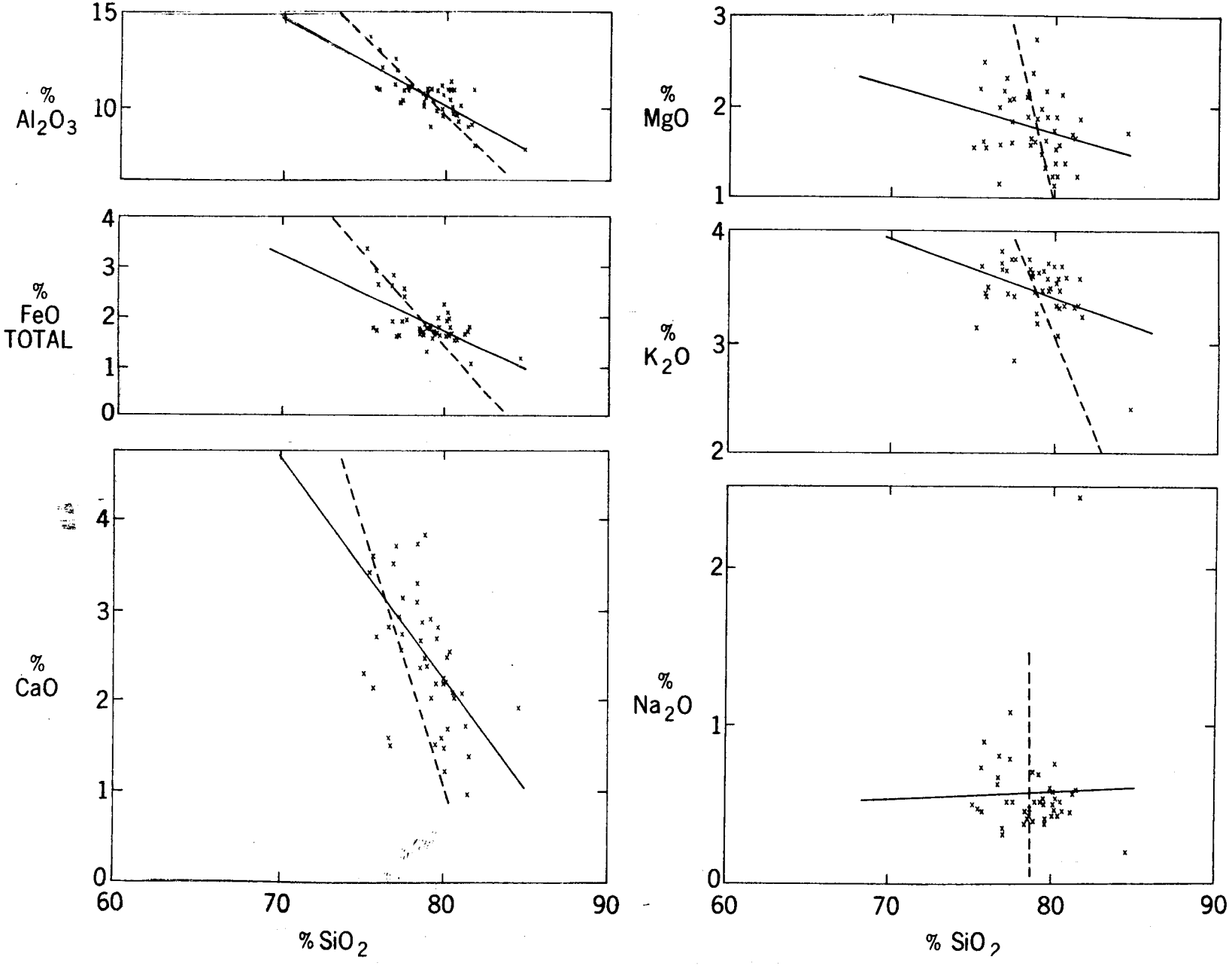
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10
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2
1
% FeO TOTAL
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2
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0
% K_2O
4
3
2
% CaO
4
3
2
1
0
% Na_2O
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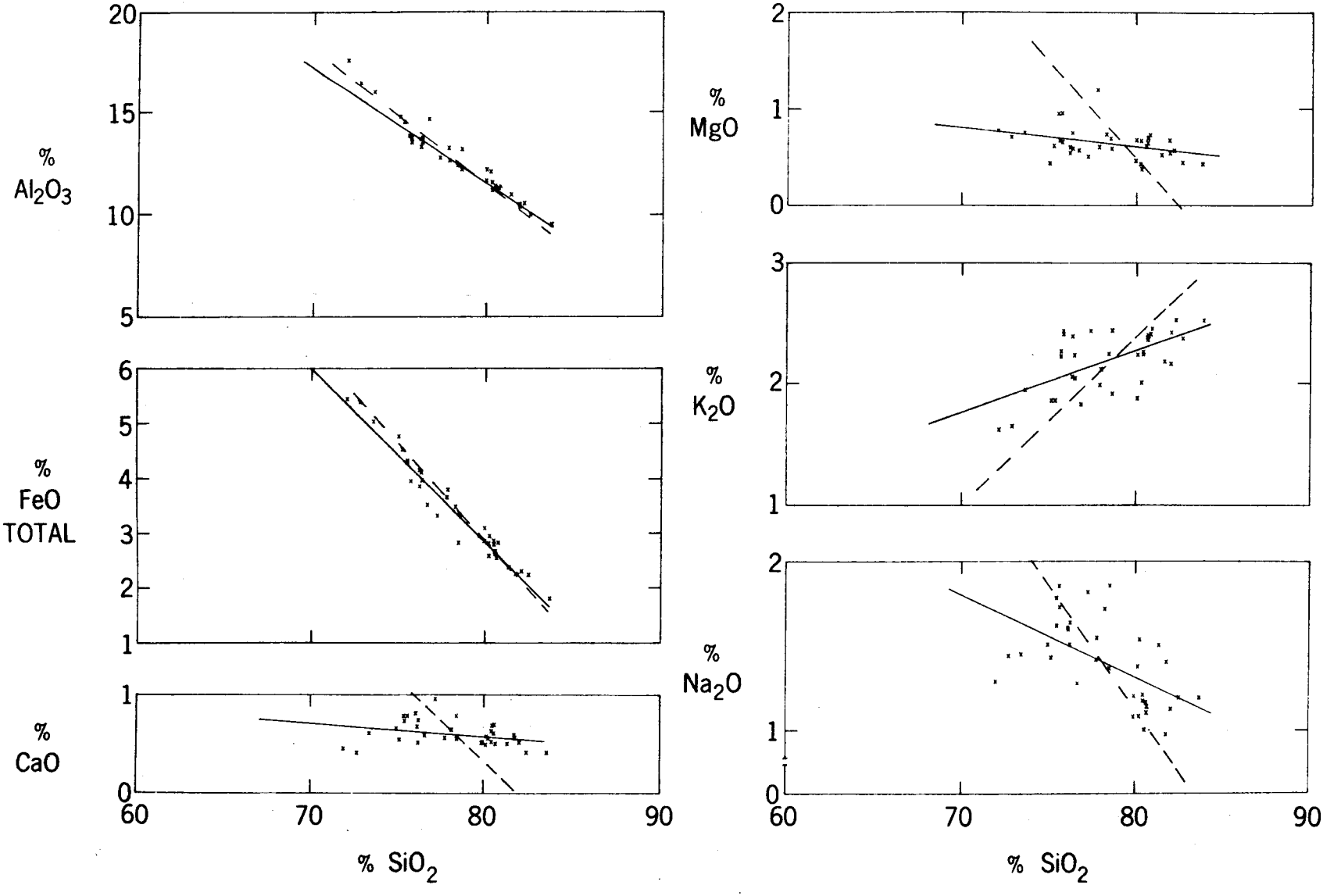
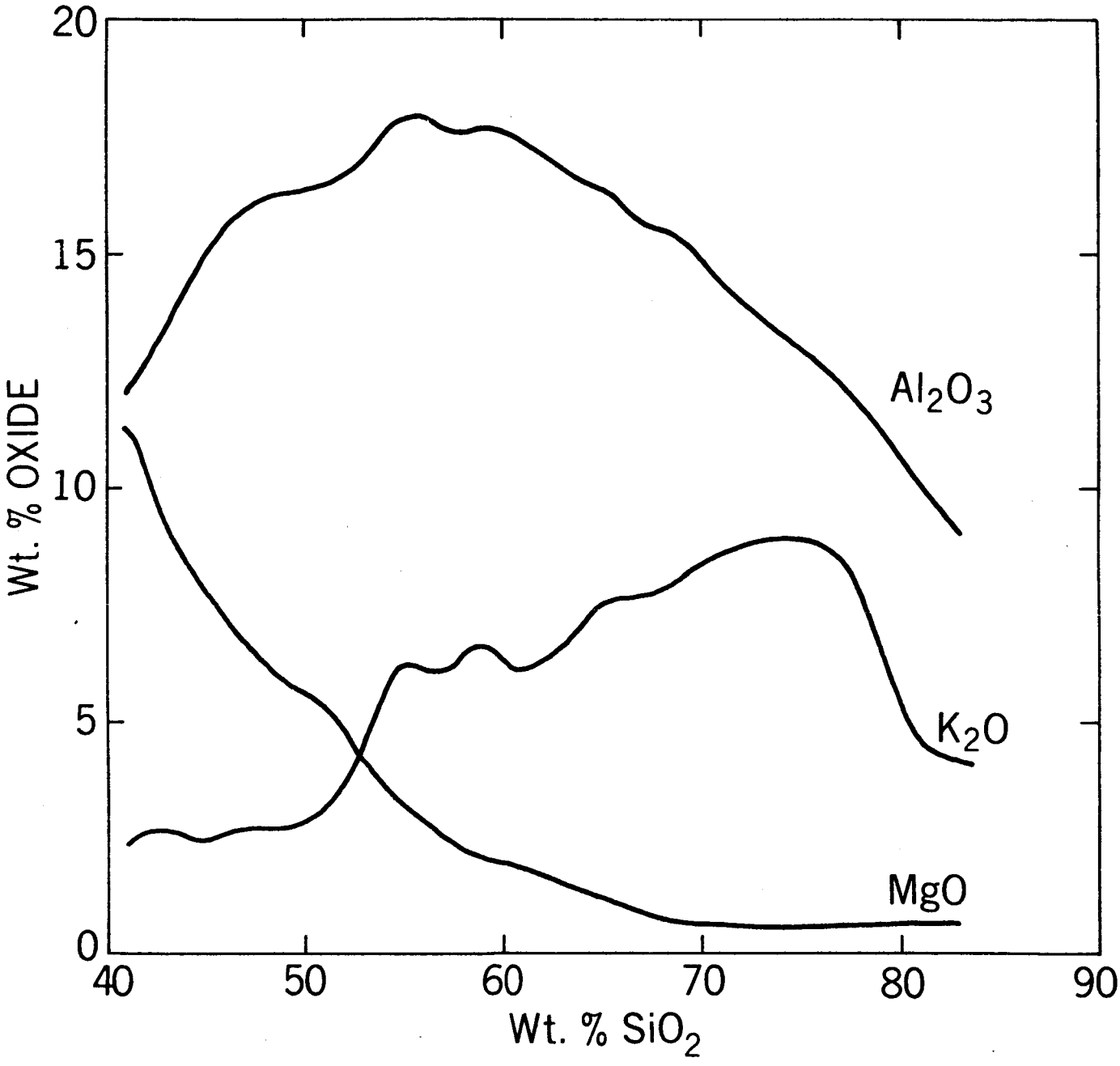
1
0
60
70
80
90
% SiO_2
60
70
80
90
% SiO_2

NORTH AMERICA

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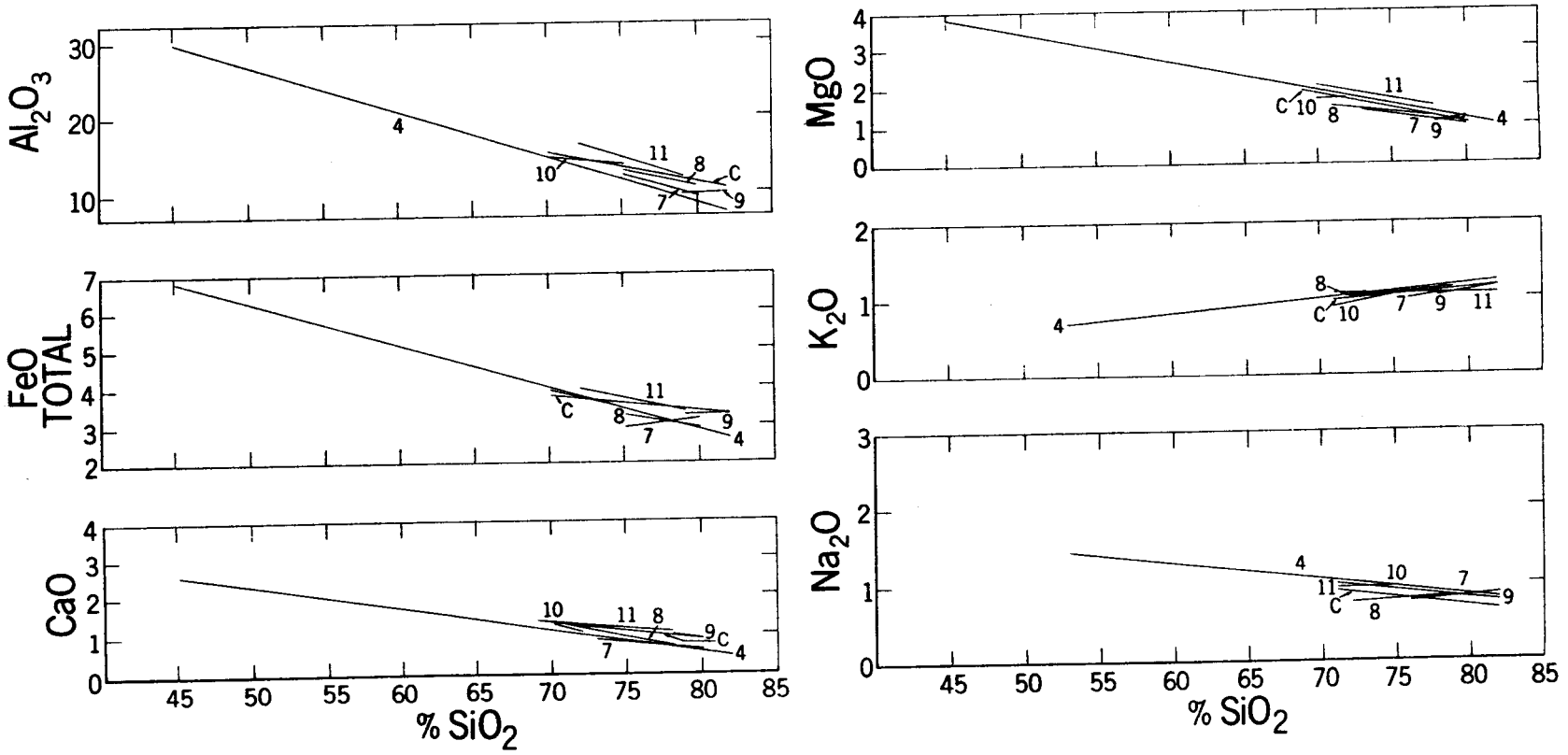
15
10
5
0
Wt. % OXIDE
40
50
60
70
80
90
Wt. % SiO2
Al2O3
K2O
MgO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FeO TOTAL
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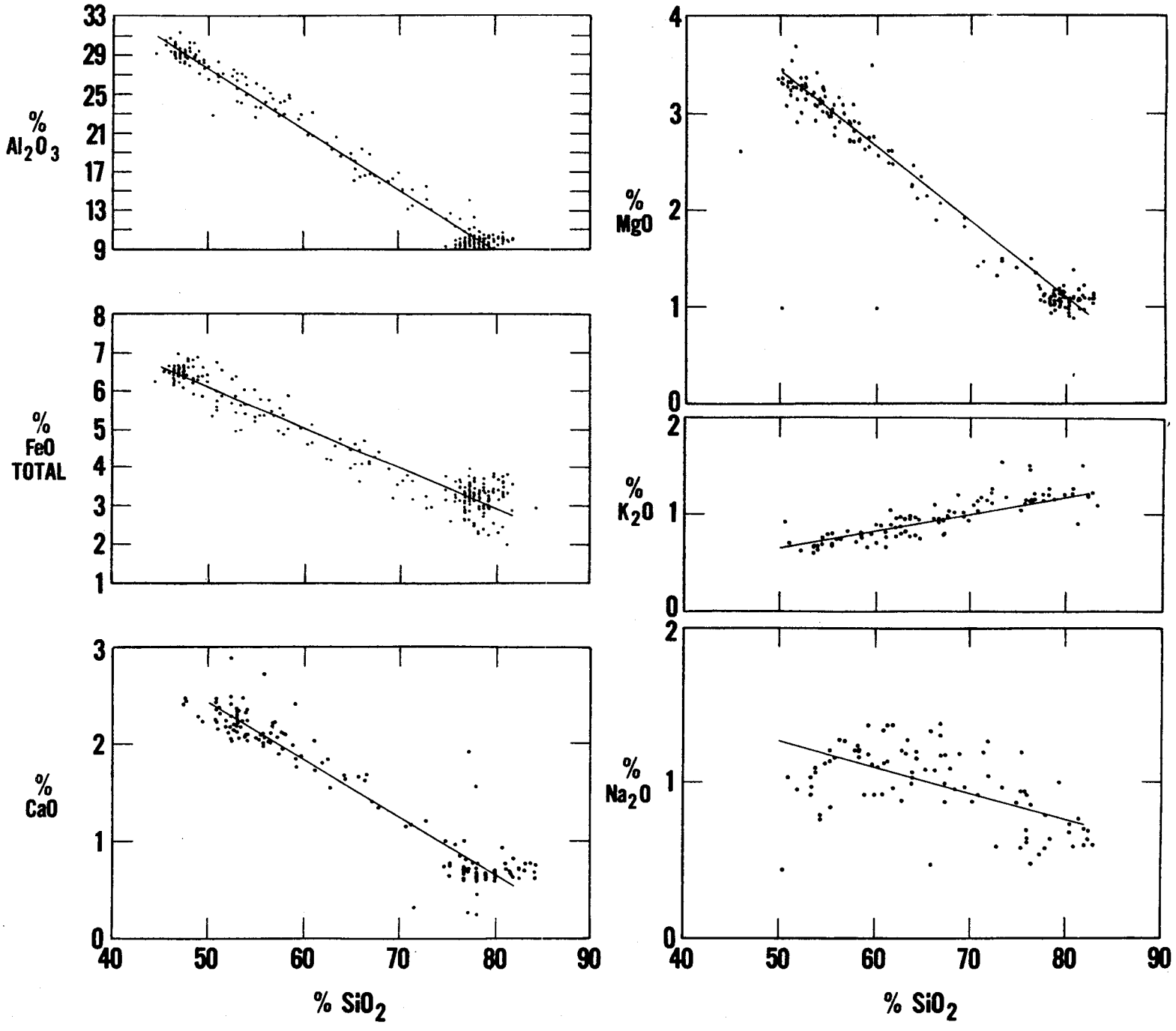
MgO
K2O
Na2O
% SiO2
% SiO2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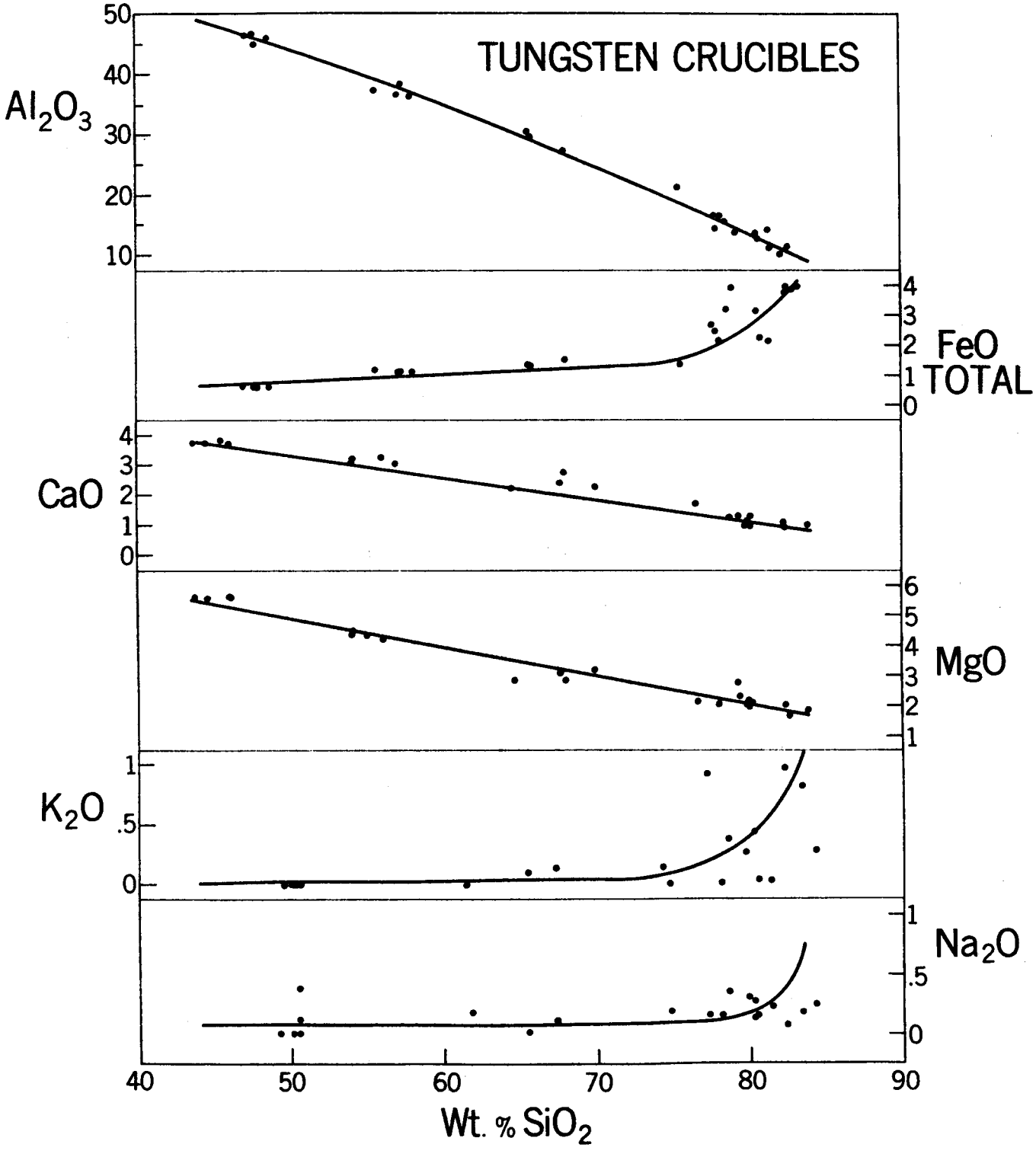
21
17
13
9
% FeO TOTAL
8
7
6
5
4
3
2
1
% CaO
3
2
1
0
40
50
60
70
80
90
% SiO_2
% MgO
4
3
2
1
0
% K_2O
2
1
0
% Na_2O
2
1
0
40
50
60
70
80
90
% SiO_2


TUNGSTEN CRUCIBLES
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30
20
10
FeO TOTAL
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3
2
1
0
CaO
4
3
2
1
0
MgO
6
5
4
3
2
1
K_2O
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Na_2O
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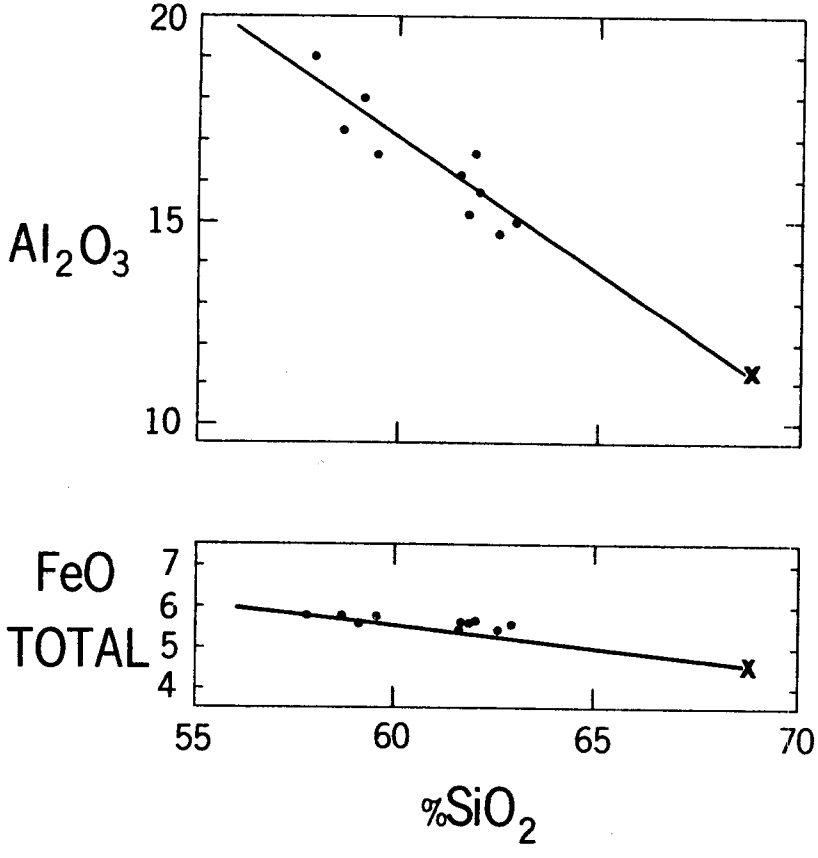
.5
0
40
50
60
70
80
90
Wt. % SiO_2

ARC WELDER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FeO
TOTAL
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6
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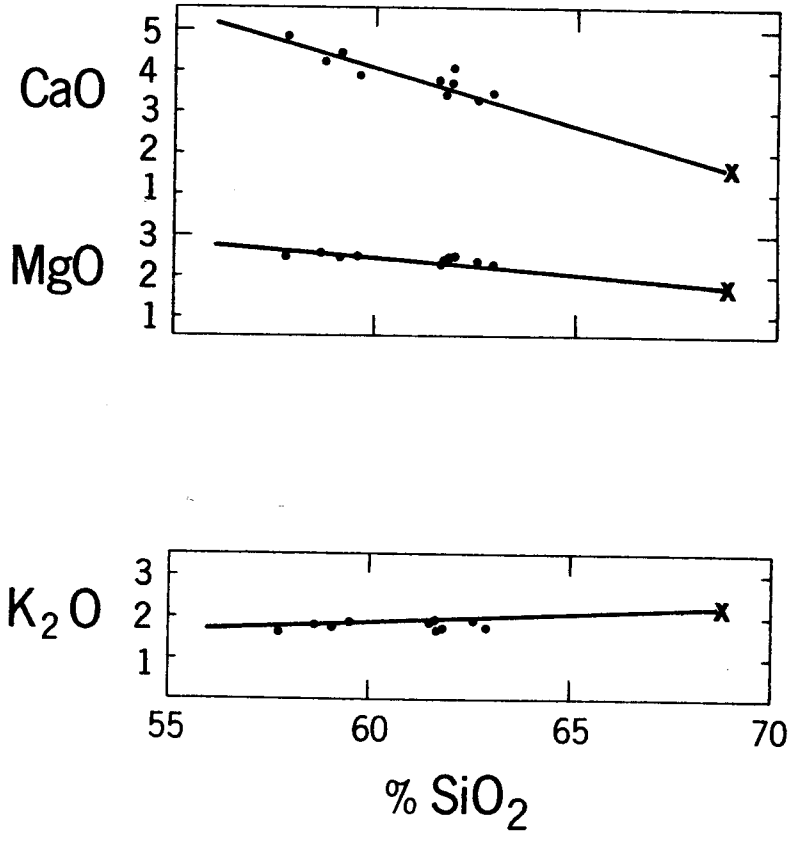
4
55
60
65
70
%SiO_2


CaO
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4
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MgO
3
2
1
K_2O
3
2
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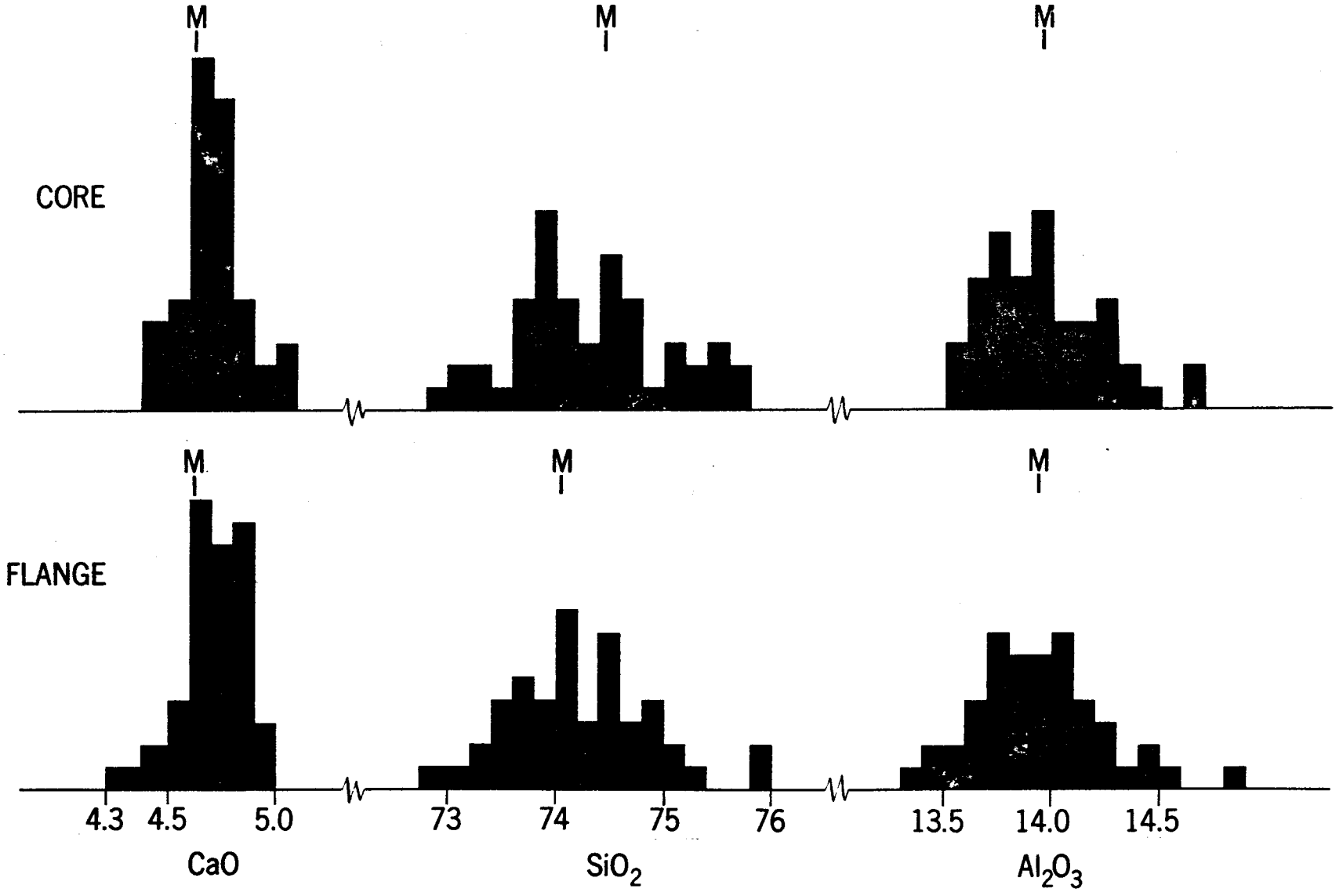
55
60
65
70
% SiO_2


M
M
M
CORE
M
M
M
FLANGE
4.3
4.5
5.0
CaO
73
74
75
76
SiO_2
13.5
14.0
14.5
Al_2O_3